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PART I: NUCLEAR MAGNETIC RESONANCE AND INFRARED INVESTIGATIONS OF LEWIS ACID-BASE INTERACTIONS

PART II: EXTENSION OF THE E AND C EQUATION TO NOVEL SYSTEMS

(Ph.D. Thesis)

Frank Luciano Slejko July 26, 1972

Part I: In this investigation, a procedure is developed by which equilibrium constants and NMR proton chemical shift changes upon complexation with a series of Lewis bases, $\Delta\omega^{\circ}$, are solved simultaneously for chloroform and other hydrogen bonding Lewis acids in non polar solvents such as cyclohexane. Enthalpies of adduct formation may be determined by measuring the equilibrium constant as a function of temperature. The enthalpies of chloroform interacting with various Lewis donors were successfully incorporated into a double-scale enthalpy equation. A linear correlation between the enthalpy and $\Delta\omega^{\circ}$ was found to exist for a limited number of donors interacting with chloroform.

Enthalpies of adduct formation for the donor quinuclidine interacting with a series of hydrogen bonding Lewis acids, determined either calorimetrically or by the NMR technique, were also incorporated into the double-scale enthalpy equation. A straight line correlation between $\Delta\omega^{\circ}$ and $-\Delta H$ for this base interacting with a series of hydrogen bonding Lewis acids was found to exist. Similar, constant base $\Delta\omega^{\circ}$ vs. $-\Delta H$ correlations were found to hold for various nitrogen, sulfur and phosphorus donors, but not for oxygen donors such as diethyl ether or tetrahydrofuran.

The magnitudes of $\Delta\omega^{\circ}$ for the protons in the Lewis acids upon hydrogen bonding to these donors are rationalized in terms of an "Electric Field Effect" arising from the lone pair electrons on the donor, E_B, and the polarizability component of the Lewis acid along the hydrogen bond, $\alpha_{//a}$. The values of $\alpha_{//a}$ for the acids studied here were obtained from their corresponding C_A and E_A parameters appearing in the double-scale enthalpy equation. For a given base interacting with a series of acids for which their $\alpha_{//a}$ values were available, a linear relationship was obtained when $\Delta\omega^{\circ}$ was plotted versus $\alpha_{//a}$. In all cases, except where the base contributed appreciably to $\Delta\omega^{\circ}$ from its neighbor anisotropy effect, a straight line resulted, even when no $-\Delta H$ vs. $\Delta\omega^{\circ}$ constant base relationship could be established.

From the slopes of these $\Delta\omega^{\circ}$ vs. $\alpha_{//a}$ plots, the "average electric fields" for the bases were obtained using an equation similar to the one originally proposed by Buckingham. The information about these donor "average electric fields" was found to be incorporated in their corresponding E_B and C_B parameters of the double-scale enthalpy equation. This model was used to account for the linear $-\Delta H$ vs. $\Delta\omega^{\circ}$ correlations and their shortcomings.

A similar approach was utilized in an attempt to explain the various correlations existing between $-\Delta H$ and $\Delta\nu$, the change in the infrared stretching vibration of a hydrogen bonding Lewis acid upon adduct formation. An electrostatic model predicted and confirmed constant base correlations between $\Delta\nu$ and $\alpha_{//a}$ for a limited set of hydrogen bonding Lewis acids.

Part II: Enthalpies of adsorption for various donors on a palladium catalyst were measured calorimetrically using a twin-cell adiabatic calorimeter. Treatment of the data with a theoretical model for the adsorption of non-electrolytes from dilute solutions on heterogeneous surfaces allowed the determination of the number of adsorption sites per gram of catalyst, the molar enthalpy of adsorption on the palladium active sites and the equilibrium constant. The molar enthalpies of adsorption were correlated using the double-scale enthalpy equation, thus allowing the determination of C_A and E_A parameter for the palladium active sites. The magnitude of these parameters suggested that the interaction with the donor molecules is mostly electrostatic.

Enthalpies of mixing between polar solutes and polar solvents were measured calorimetrically as a function of solute concentration. From these measurements, the enthalpies of mixing for the solute at infinite dilution in the solvents were calculated. Attempts to correlate these data with a double-scale enthalpy equation failed. Various other models were also unsuccessful in predicting the enthalpies of mixing.

SPECTROSCOPIC STUDIES OF INORGANIC COMPLEXES

Robert Ling Chiang July 27, 1972

Introduction

Physical methods have been widely used in the inorganic systems. These kinds of measurements can give us the information not only about the interactions in the molecules, but also the structure of the molecules. In this work, an attempt was made to correlate the spectrochemical results with the interactions between metal ion and ligands. It has also been tried to interpret the results with the model obtained from Lewis acid-base studies, the interactions between metal ion and ligands can be treated as a special case of Lewis acid-base interactions.

A. Spectrochemical Studies on Some Tetragonal NiL_2X_2 Complexes

The system reported here consists of complexes of the form NiL_2X_2, where L represents ammonia, aniline, water or pyridine ligands and X represents chloride or bromide. In each of the complexes, the metal ion is surrounded by four bridged halide ions forming a polymeric chain and by two other ligands giving six-coordination about the nickel(II) atom. The site symmetry is assumed to be D_4h and electronic spectra fit this model.

A computer program was developed to calculate a reliable set of crystal field parameters provided that the number of transition bands is greater than the number of the parameters. When L changes, the electronic spectrum changes as well as the calculated parameters which indicate the changing of the bonding or geometry of the complex and the ligand strength at axial position.

The calculated D_q^{xy}, which is the ligand strength on the xy plane, remain practically constant except for $Ni(H_2O)_2Cl_2$. The difference is resulted from a significant change of molecular structure because of hydrogen bonding. The bridging halides have less electron density to participate in the antibonding interaction. Consequently, D_q^{xy} is larger than the D_q of the terminal halides.

As might be expected from the inductive effect of the four bridging halides, D_q^z, which is the ligand strength along z axis, is smaller than the values for some ligand in octahedral complexes except for D_q^z of water in $Ni(H_2O)_2Cl_2$.

B. EPR Studies of Lewis Acids and Bases Interactions

Bis-(hexafluoroacetylacetonato) Cu(II) is the first complex which has been successfully treated as a Lewis acid. The enthalpies of addition with variety bases were measured and can be correlated to a double scale equation proposed by Drago and Wayland:

$$-\Delta H = C_A C_B + E_A E_B \qquad (1)$$

where C_A, E_A are assigned to each acid and C_B, E_B are assigned to each base. The E value was first interpreted as the susceptibility of acid or base to undergo electrostatic interaction and C value was interpreted as the susceptibility of acid or base to form covalent bond.

It is found that A_{av}, isotropic hyperfine coupling constant, has no relation with enthalpies of formation, but decreases as E_B or C_B increases. A model has been proposed to explain the result. Assuming that E and C have their physical meaning as previously proposed and incoming base is along z axis, ligand field theory using first order perturbation treatment and MO approximation predicts that A_{av} does decrease as E_B or C_B increases. The model was successfully extended to explain the substituent effect of Cu(II) acetylacetonates.

The results are not conclusive, but encouraging in explaining the real meaning of those parameters.

D. Kinetic Studies of Chemical Reactions by Calculation of Exchange-Broadened NMR Lineshapes

$Ni(DPM)_2$ is an ideal complex which can be treated as Lewis acid except that it forms two-base adducts with various bases. However, the enthalpies of formation for one-base adduct can be obtained indirectly by kinetic studies of exchange reaction of the two-base adducts with excess free base in the solution.

The effect of exchange on the NMR signal has been studied extensively in both diamagnetic and paramagnetic systems. In this work, both line-width method and line-shape method were used. The line-width equations were derived from Bloch formularism. In the slow exchange region, the equation can be simplified so that the modified line-width at peak half height is proportional to the rate of exchange reaction.

The line-shape equations were derived using quantum mechanical density matrix treatment. The advantage of this method is that spin-spin coupling between the protons can be considered. Also, it handles the non-coupled protons as well as the classical derivation. A computer program was developed to calculate the line shape of AB or A_2B system in intermolecular exchange reaction. The rate of exchange reaction can be obtained by varying rate in the calculation to obtain the best fit with the experimental results.

Three systems have been studied. The activating enthalpies for one base dissociation process are 14.1 kcal/mole for 4-methyl pyridine adduct, 13.1 kcal/mole for 4-picoline N-oxide adduct, and 10.9 kcal/mole for DMSO adduct. Assuming that the reaction is SN1 and rate determine step is dissociation process, the enthalpy of formation of two-base adducts for 4-picoline with $Ni(DPM)_2$ is 18.6 kcal/mole. According to the model proposed, in which the enthalpy of formation of one-base to two-base adduct equal to the activating enthalpy of the exchange reaction, the enthalpy of one base adduct is equal to 4.5 kcal/mole.

The contact shift of t-butyl group with respect to different bases has been studied. It is also found that the contact shift decreases as E_B or C_B increases. This result can be easily explained using the model previously proposed.

George F. McKnight July 31, 1972.

STUDIES OF COMPOUNDS AND REACTIONS OF THE OCTACYANOMOLYBDATE(IV) ION.

Part I. Divalent First Row Transition Metal Compounds of $Mo(CN)_8^{4-}$.

Transition metal cyanide compounds have long been of interest to the inorganic chemist. The compounds vary in complexity from the simple monocyanide compound of Ag^+ to the more involved octacyanide compounds of tungsten, molybdenum and rhenium. Although cyanide compounds show great structural variety a large number of these compounds are similar in that they exist as polymers with the cyanide ligand acting as a bridging group between metal ions. A great deal of work has been done in determining the structures of the simpler cyanide complexes but very little has been done with regard to structural studies of the eight-coordinated cyanide compounds. In an effort to obtain further information about the structures of the octacyanide compounds a series of divalent first row transition metal compounds of the octacyanomolybdate(IV) ion were prepared and studied.

Potassium octacyanomolybdate(IV) dihydrate, $K_4Mo(CN)_8 \cdot 2H_2O$, has been shown to exist as a slightly distorted dodecahedron in the solid state.[1] The compound is extremely soluble in aqueous solution. In solution the structure fo the octacyanomolybdate(IV) ion is uncertain. Experimental evidence indicating a dodecahedral structure has been found[2]. However evidence indicating a square antiprismatic structure has also been found[3]. The divalent transition metal compounds of the octacyanomolybdate(IV) ion, $M_2Mo(CN)_8 \cdot xH_2O$ (where $M^{++} = Zn^{++}$, Cu^{++}, Co^{++}, Ni^{++}, Fe^{++}, Mn^{++} and x= 2-8) are all extremely insoluble in water as well as all other common solvents. This extreme insolubility is a good indication that the compounds are polymers of some type.

The infrared spectra of these compounds in the cyanide stretching region (2000 to 2200cm^{-1}) consists of single broad bands (50 to 75cm^{-1} at half peak height) betweem 2135cm^{-1} and 2170cm^{-1}. These single broad bands differed quite drastically from the spectrum of the parent potassium compound which consists of four sharp peaks with the main peak appearing at 2104cm^{-1}. Both the broadening of the cyanide stretching band and its shift to higher frequency on precipitation with the divalent transition metal cations are indicative of bridging of the cyanide ligand. This has been found for the chromicyanides, cobalticyanides and ferrocyanides[4] as well as for the adduct, $K_4Mo(CN)_8 \cdot 8BF_3$[5], all of which are known to contain bridged cyanide groups.

Magnetic susceptibility studies yielded some information with regards to the environment of the metal cations of these compounds. All of the compounds except the Zn^{++} compound exhibit some degree of paramagnetism:

The magnetic moments calculatedfall within the experimental range found for the particular cation when in a weak tetrahedral or octahedral field. Except for the Mn^{++} compound all of the moments are higher than the spin-only values expected, indicating an orbital angular momenta contribution to the moments. The size of the orbital angular momentum contribution indicated that in the Co^{++} and Ni^{++} compounds the cations were most likely surrounded by an octahedral field.

To summarize, the work thus far indicates that these divalent transition metal compounds of the octacyanomolybdate(IV) ion exist as polymers where the cyanide ligand acts as a bridge between the Mo(IV) ion and the metal cations. It is also believed that the metal cation in the Ni^{++} and Co^{++} compounds existsin an octahedral environment.

Part II. Kinetics and Mechanism of the Reaction of $HCrO_4^{1-}$ with $Mo(CN)_8^{4-}$ in Acid Solution.

The kinetics and mechanisms for reductions of Cr(VI) to Cr(III) using various reducing agents have received a great deal of attention from both the organic and inorganic chemist. The relative stability of the reacting Cr(VI) species as well as the characteristic inertness of the Cr(III) species produced have allowed detailed mechanistic studies of the reduction of Cr(VI) to Cr(III). For one-electron reducing agents (into which category the majority of the transition metal reducing agents fall) the mechanism can be generalized as shown in Scheme I. That is to

Scheme I

$$\text{Red} + \text{Cr(VI)} \rightleftharpoons \text{Ox} + \text{Cr(V)}$$

$$\text{Red} + \text{Cr(V)} \rightleftharpoons \text{Ox} + \text{Cr(IV)}$$

$$\text{Red} + \text{Cr(IV)} \rightleftharpoons \text{Ox} + \text{Cr(III)}$$

say, the reduction proceeds by a series of three one-electron transfer steps. The majority of the one-electron reducing agents have been of the octahedral variety. Little has been done with regard to one-electron eight-coordinated species as reducing agents. To gain further knowledge in this area a study of the reduction of $HCrO_4^{1-}$ by $Mo(CN)_8^{4-}$ was undertaken.

Stoichiometrically the reaction follows equation (1). The exact nature of the Cr(III) product could not be ascertained. However it is

$$HCrO_4^{1-} + 3Mo(CN)_8^{4-} + 7H^+ \longrightarrow Cr(III) + 3Mo(CN)_8^{3-} + 4H_2O \qquad (1)$$

certain that most of the Cr(III) is tied up in a highly ngatively charged polynuclear complex with either $Mo(CN)_8^{3-}$ or $Mo(CN)_8^{4-}$ or both. The existence of the neutral complex, $CrMo(CN)_8$ could not be disproven.

Kinetically, the reaction was found to have a first order dependence on $HCrO_4^{1-}$ and $Mo(CN)_8^{4-}$, a zero order dependence on $Mo(CN)_8^{3-}$ and an approximately second order dependence on H^+. The kinetics are consistnet with the second order rate expression shown in equation (2). This implies that the reduction of Cr(VI) to Cr(V) in Scheme I is the rate determining step. The second order rate constant was shown to have a value of *ca.* 10 M^{-1} sec^{-1}. The rate constant is substantially lower than

$$-d\ HCrO_4^{1-}/dt = k_2\ HCrO_4^{1-}\ Mo(CN)_8^{4-} \qquad (2)$$

that found for most other one-electron reducing agents of the transition metal variety. It is possible that the low rate results from the relatively poor complexing ability of $Mo(CN)_8^{4-}$. This presupposes the existence of a preequilibrium involving oxidant and reductant prior to reduction.

The study of the reduction of $HCrO_4^{1-}$ by $Mo(CN)_8^{4-}$ indicates that in most respects the reaction parallels what has been found for reducing agents of coordination number eight. A possible explanation for the low second order rate constant could be the existence of a preequilibrium prior to reduction in which case the K_{eq} could be a determining factor as to the size of the rate constant.

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STUDIES OF TRANSITION METAL CYCLOPROPENYL COMPLEXES

W. Karl Olander August 22, 1972

Introduction

The cyclopropenyl cation, $C_3R_3^+$, obeys the aromaticity rule of 4n + 2 π-electrons, where n = 0, and from simple Huckel Molecular Orbital Theory is predicted to be stable.[1] Following Breslow's[2] initial report of the synthesis of $C_3(C_6H_5)_3^+$ in 1957, the list of cyclopropenyl cations has grown steadily, exceeding thirty at present.

The synthesis of the first C_3R_3-metal complex, trihaptotriphenylcyclopropenyl nickel carbonyl bromide, 1, was described by Gowling and Kettle in 1964.[3] $[(h^3\text{-}C_3(C_6H_5)_3)Ni(CO)Br]$ was proposed to exist as a halide bridged dimer. Single crystal X-ray data for $[(h^3\text{-}C_3(C_6H_5)_3)Ni(py)_2Cl]\cdot py$[4] and $[h^3\text{-}C_3(C_6H_5)_3)Ni(h^5\text{-}C_5H_5)]$[5] confirm a π or trihapto orientation of $C_3R_3^+$ with respect to nickel.

Relatively little is known about the solution chemistry of the triphenylcyclopropenyl complexes due to their overall low solubility and the consequent lack of a suitable method, e.g., nmr or ir, for monitoring reactions. Because of the insufficient information concerning the phenyl derivatives, a study employing alkylcyclopropenyl ligands was undertaken. The results of that research are summarized in the following sections.

Results

A series of complexes $[(h^3\text{-}C_3(\underline{t}\text{-}C_4H_9)_2R)Ni(CO)Br]$, where R = methyl (2), phenyl (3), and tert-butyl (4), was prepared according to equation 1. From infrared considerations 2-4 are believed analogous to Gowling and Kettle's compound, 1. The experimental

$$[C_3R_3]Br \;+\; Ni(CO)_4 \longrightarrow [(h^3\text{-}C_3R_3)Ni(CO)Br] \;+\; 3CO \qquad (1)$$

and calculated molecular weights (parentheses) for 3 and 4 determined by osmometry in benzene are 321, 342 (394) and 332, 337 (373),

respectively. The mass spectrum of 4 at 100° (10 or 70 eV) shows no ions derived from CO-containing species but exhibits strong peaks corresponding to tri-*tert*-butylcyclopropenyl nickel bromide dimer, $[(h^3\text{-}C_3(\underline{t}\text{-}C_4H_9)_3)NiBr]_2$.

Addition of CO to a methylcyclohexane solution of 4 (ν_{CO} 2052 cm^{-1}) results in the rapid equilibria shown in equations 2 and 3.

$$C_3(\underline{t}\text{-}C_4H_9)_3Ni(CO)Br + CO \longrightarrow C_3(\underline{t}\text{-}C_4H_9)_3Ni(CO)_2Br \qquad (2)$$

$$C_3(\underline{t}\text{-}C_4H_9)_3Ni(CO)_2Br + 2CO \longrightarrow Ni(CO)_4 + [C_3(\underline{t}\text{-}C_4H_9)_3]Br \qquad (3)$$

Carbonyl bands appear at 2089 (s), 2060 (s), 2055 (s) and 2044 cm^{-1} (m-s), The two highest energy bands, which appear together, are assigned to tri-*tert*-butylcyclopropenyl nickel dicarbonyl bromide, 5. $Ni(CO)_4$ was isolated from solution by prolonged passage of CO and trapping the volatile components in a Dry Ice/acetone bath. The band at 2044 cm^{-1} is due to $Ni(CO)_4$. The band at 2055 cm^{-1}, shifted slightly by overlap with adjacent bands, is assigned to 4. In polar solvents in the absence of added CO, 5 is formed from 4 through a slight amount of disproportionation.

Addition of $[C_3(C_6H_5)_3]BF_4$ to a methanolic solution of 4 results in the formation of analytically pure $[(h^3\text{-}C_3(C_6H_5)_3)Ni(CO)Br]$ as a precipitate after one hour at room temperature.

Thermal decarbonylation of 4, effected by heating under vacuum at 80° for 30 hours, yields $[(h^3\text{-}C_3(\underline{t}\text{-}C_4H_9)_3)NiBr]_2$, 6, as a red air-sensitive solid. Addition of CO to a hexane solution of 6 establishes the equilibria in equations 2 and 3. In the presence of bidentate ligands, 6 is converted to chelate adducts of the type $[(h^3\text{-}C_3(\underline{t}\text{-}C_4H_9)_3Ni(L\text{-}L)Br]$, where L-L can be diphos, dipy, en or phen. No exchange of free and coordinated $C_3(\underline{t}\text{-}C_4H_9)_3^+$ with 6 in pyridine could be detected at 100° from the ^1H nmr.

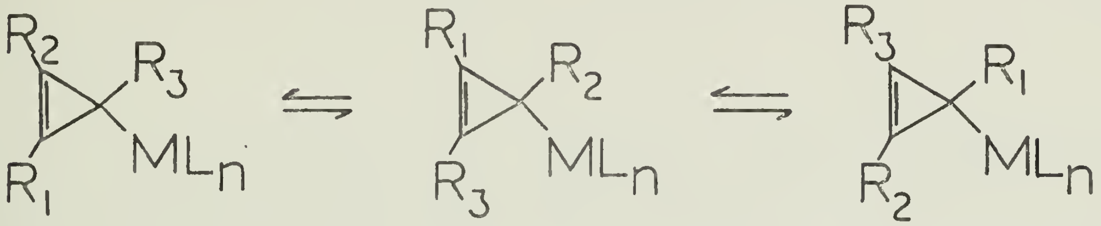
Complexes 2-4 are readily converted to mixed *pentahapto*cyclopentadienyl sandwich compounds $[(h^3\text{-}C_3(\underline{t}\text{-}C_4H_9)_2R)Ni(h^5\text{-}C_5H_5)]$, where R = methyl (7), phenyl (8), and *tert*-butyl (9), by the reaction

$$(h^3\text{-}C_3R_3)Ni(CO)Br + NaC_5H_5 \longrightarrow (h^3\text{-}C_3R_3)Ni(h^5\text{-}C_5H_5) + CO + NaBr \quad (4)$$

in equation 4. The air-stable solids, 7-9, are purified by sublimation. The mass spectrum of 9 exhibits prominent peaks at m/e 330,

332 (molecular ion); 273, 275 $(C_3(\underline{t}\text{-}C_4H_9)_2NiC_5H_5)^+$; 207 $(C_3(\underline{t}\text{-}C_4H_9)_3)^+$; and 57 $(\underline{t}\text{-}C_4H_9)^+$.

*Monohapto*cyclopropenyl complexes, $[(h^1\text{-}C_3R_3)ML_n]$ may exhibit fluxional character in solution (equation 5).[6,7] This phenomenon



(5)

is well suited to study using variable temperature nmr techniques. Reaction of $[C_3(\underline{t}\text{-}C_4H_9)_3]BF_4$ with $NaMn(CO)_5$ in THF at -15° results in the formation of orange crystals of $[C_3(\underline{t}\text{-}C_4H_9)_3]Mn(CO)_5$, **10**. Nmr and ir data make reasonable the assignment of **10** as ionic and not $[(h^1\text{-}C_3R_3)Mn(CO)_5]$. At room temperature the ir spectrum of **10** shows bands in addition to $Mn(CO)_5^-$ which can be interpreted as a *monohapto* interaction between the C_3-system and $Mn(CO)_5^-$. **10** decomposes rapidly in polar solvents at room temperature to yield $Mn_2(CO)_{10}$ and $[C_3(\underline{t}\text{-}C_4H_9)_3]_2$ and $C_3(\underline{t}\text{-}C_4H_9)_3H$. The same reaction with $NaMn(CO)_5$ and $[C_3(C_6H_5)_3]BF_4$ gives $Mn_2(CO)_{10}$ and $[C_3(C_6H_5)_3]_2$.

Bonding in $(h^3\text{-}C_3R_3)M$

The chemistry of cyclopropenyl closely parallels that of the allyl ligand except in the ease with which $C_3R_3^+$ forms *monohapto* complexes. For many of the complexes discussed the corresponding h^3-allyl complex is known.[8,9,10]

Electrostatically $C_3R_3^+$ would be expected to be a poor Lewis base, but it could back-bond effectively using its E symmetry orbitals. The ^1H nmr spectra of coordinated tri-*tert*-butylcyclopropenyl exhibits an upfield shift of from 12-25 Hz compared to the uncomplexed ligand.

From nmr considerations and the close resemblance to allyl, $C_3R_3^+$ can best be described as occupying two coordination positions around nickel. In this context $[(h^3\text{-}C_3R_3)Ni(CO)Br]$ and $[(h^3\text{-}C_3R_3)NiBr]_2$ are proposed to be square planar. The geometry of complexes formed by the addition of other ligands, e.g., **5**, or chelates,

$[(h^3\text{-}C_3R_3)Ni(L\text{-}L)Br]$, is thought to be iso-structural with the square pyramidal structure found for $[(h^3\text{-}CH_2C(CH_3)CH_2)Ni(diphos)Br]$.[9]

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MATRIX ISOLATION SPECTROSCOPY AND ITS APPLICATIONS TO INORGANIC CHEMISTRY

Jim D. Atwood October 3, 1972

Matrix isolation is a technique for trapping molecules as isolated entities in an inert solid in order to investigate their properties.[1] The technique was introduced when Pimentel and co-workers reported the isolation and study by infrared spectroscopy of several hydrogen-bonded species in 1954.[2] Most of the early work involved the study of free radicals, which led to the development of matrix isolation electron spin resonance spectroscopy.[3] The field of unstable molecular species was opened to matrix isolation spectroscopy with Linevsky's work incorporating a Knudsen effusion cell into the system such that high temperature species could be generated and then quenched in the inert matrix.[4]

Sample deposition is very important in matrix isolation work. Very slow deposition (6-12 hours) employing very high matrix gas to solute ratios (1000/1) is necessary for good isolation of the reactive species. In working with simple organic gases, Rochkind found that a pulsed deposition technique for a few minutes not only worked, but provided clearer spectra than the slower deposition.[5] He was able to do both qualitative and quantitative analysis of mixtures of the gases with the pulsed matrix isolation spectroscopy,[5,6] but the technique has not yet been applied to highly reactive species.

Infrared spectroscopy has been the most widely used method for investigating trapped species. Pimentel's early work, the adaptibility of the infrared optics to matrix isolation, and the very small matrix shifts are the main reasons that infrared spectroscopy is used so frequently in matrix isolation work.

The ultraviolet-visible technique was used more in the early work than it is at present. The main difficulty is that matrix effects on the spectra are more important than they are in infrared spectroscopy. Despite this difficulty, ultraviolet-visible spectroscopy has been used to determine the groundstates in transition metal compounds.[7]

Electron spin resonance has been used, but its use is complicated by magnetic anisotropies and matrix site effects.[3] These complications have led to the use of electron spin resonance to investigate matrix effects.[8]

Raman spectroscopy has been the most recent area to develop.[9] Ozin has followed the initial work with studies of many different types of molecules,[1c] and it appears that matrix isolation Raman spectroscopy will complement matrix isolation infrared spectroscopy.

A recent development, applying the Varian CATV 1024 time averaging computer to matrix isolation Raman spectra, is reported by Andrews to give an improved signal-to-noise ratio.[10]

A large amount of the work done in matrix isolation has been in the determination of physical properties--structure and groundstates. As examples, I have chosen: the study of trimetal carbonyl species that led to the first reported spectrum of $Fe_3(CO)_{12}$ in C_{2v} structure;[11] DeKock and Gruen's work, in which they experimentally justified their assignment of the groundstates of the transition metal dichlorides using ultraviolet matrix isolation spectra;[7a] and the electron spin resonance work on $Cu(NO_3)_2$ and CuF_2 that produced evidence for orientation of the solute in the matrix.[12]

The other major area of application has been in synthesis of species that are unstable at higher temperatures. The synthesis of uranium carbonyls was accomplished by allowing controlled diffusion of carbon monoxide in an argon matrix,[13] and the same technique has since been applied to the platinum and palladium carbonyls.[14] In another series of preparations, Andrews prepared LiO_2, NaO_2, KO_2, RbO_2, and LiN_2 and analyzed them by isotopic shifts in the infrared spectra, finding the results consistent with C_{2v} symmetry.[15]

From the examples given, it is obvious that matrix isolation spectroscopy is applicable to a wide variety of molecular species which can be extensively studied by a combination of the four spectroscopic techniques.

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PHOTOCHEMICAL SMOG FORMATION

Martin A. Cohen October 24, 1972

Introduction

Materials that are emitted into the atmosphere are subjected to a number of interesting and unusual reactions. These reactions lead to many products whose deleterious effects[1,2,3] have been recognized as one of the most pressing problems in urban areas throughout the world.[4,5,6,7] Our present knowledge of the chemistry of the reactions involved in photochemical smog formation is based primarily on laboratory experiments simulating atmospheric conditions and on using this data to propose mechanisms to account for these observations. However, these mechanisms have not satisfactorily dealt with the problem in its entirety. This seminar will summarize the recent studies of the oxides of nitrogen, to be designated as NO_x, and hydrocarbon pollutants, which form what is commonly referred to as Los Angeles smog, a chemically oxidizing atmosphere which occurs on clear days having low humidity and an overhead inversion.

Oxides of Nitrogen

Under the high temperature conditions which are found in an internal engine, direct combination of N_2 and O_2 can occur,[8] giving rise to the formation of NO, a primary pollutant in automobile exhaust gases. Since there is a high local concentration of NO in the exhaust fumes, further reaction of the NO can occur with O_2 as shown:

$$2NO + O_2 \rightarrow 2NO_2$$

giving rise to NO_2[9] which is the primary chain-initiating reagent for photochemical smog. No ultraviolet radiation below 290 nm. reaches the lower atmosphere because of its absorption by O_3 in the upper atmosphere. Nitrogen dioxide is then the only major species in the lower atmosphere which can absorb the available ultraviolet radiation. Upon absorption, NO_2 will photodissociate into NO and oxygen atoms (equation 1 in the appendix). It is this photodissociation which is believed to initiate all further reactions of airborne pollutants. Further reactions of these species will be discussed including a steady state approximation.

Mixtures of Hydrocarbons and NO_x

Having established the presence of a steady state situation involving the oxides of nitrogen, further reactions with hydrocarbons must be considered.[10,11,12,13] The presence of hydrocarbons in the atmosphere arises from the incomplete combustion of petroleum fuels in mechanical engines and from the evaporation from the storage areas for the hydrocarbons. It has been known for a considerable time that

the final reaction products in photochemical smog are aldehydes ketones, ozone, and peroxyacyl nitrates (PAN).[14] Also, it has been observed, both in the atmosphere and model systems studies, that (1) hydrocarbons are oxidized and disappear from the system, (2) secondary pollutants (those arising from the atmospheric reactions) appear, (3) NO is oxidized to NO_2, and (4) ozone is formed when all the NO has disappeared. It has become desirable to postulate mechanisms which can handle sufficiently these observations. Several investigators[1,15,16,17,18] have concluded that the initiation step involves the hydrocarbon molecule reacting with the oxygen atom to give free radicals and other products. These free radicals include $\cdot OH$, $\cdot R$, where R is an alkyl group, $RO_2\cdot$, and $HO_2\cdot$. Secondary chain propogation may involve an oxide of nitrogen. Finally, these radicals are lost by chain terminating steps, of which reaction with NO_2 will be the primary route of concern today.

Conclusions

With the increasing demands placed upon our limited atmosphere, it becomes imperative to have a better understanding of the photochemical reactions occurring in the air. Based on our present understanding, it has been shown that, in the absence of NO_2, no formation of aerosols, eye irritant, or new phototoxins can occur. Thus, it is imperative that NO_2 emissions be controlled.[19] Hydrocarbons, too, must be controlled, for with the NO_x mixtures, there is an interdependence of reaction. Together, they influence the quality of the air each person must breathe.

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Appendix

A Generalized Fifteen Step Mechanism for Photochemical Smog[18]

1. $NO_2 + h\nu \rightarrow NO + O$
2. $O + O_2 + M \rightarrow O_3 + M$
3. $O_3 + NO \rightarrow NO_2 + O_2$
4. $O_3 + NO_2 \rightarrow NO_3 + O_2$
5. $NO_3 + NO_2 \xrightarrow[H_2O]{} 2HNO_3$
6. $NO + NO_2 \xrightarrow[H_2O]{} 2HNO_2$
7. $HNO_2 + h\nu \rightarrow \cdot OH + NO$
8. $CO + \cdot OH \rightarrow CO_2 + HO_2\cdot$
9. $HO_2\cdot + NO \rightarrow NO_2 + \cdot OH$
10. $HO_2\cdot + NO_2 \rightarrow HNO_2 + O_2$
11. $Hc + O \rightarrow \alpha RO_2\cdot$
12. $Hc + O_3 \rightarrow \beta RO_2\cdot + \gamma RCHO$
13. $Hc + \cdot OH + \rightarrow \delta RO_2\cdot + \epsilon RCHO$
14. $RO_2\cdot + NO \rightarrow NO_2 + \theta \cdot OH$
15. $RO_2\cdot + NO_2 \rightarrow PAN$

RARE EARTH LIQUID LASERS

Gretchen Hall October 31, 1972

Laser operation is based on the action of spontaneously emitted photons which cause the stimulated emission of other photons. The laser action will only occur when there is a population inversion between the emitting level and the terminal level of the transition. Schawlow and Townes have related the minimum population inversion necessary to the emission wavelength, quantum yield, and other properties of the emitting system and also to several parameters of the laser cavity.[1] This cavity must be designed to allow the amplification of the radiation with minimum losses.[2]

Liquid lasers have several advantages over other laser systems.[3] The construction is less expensive and there is also no problem of heat dissipation. Compared to gaseous systems, the liquid systems can have a greater concentration of active material. The problem of light scattering in liquid lasers due to large temperature gradients has been solved by circulation of the liquid through a heat exchanger.[4,5]

Rare earth ions are used in many solid and liquid lasers.[2] The f-f transitions involved in the emissions are not greatly influenced by the ion's surroundings, and so the bandwidths are small.

Chelate laser

The first liquid laser was the rare earth chelate laser, a result of work started by Weissman in 1942,[6] and extended by Crosby.[7-9] Among the rare earth ions, Eu(III) was best suited for laser action.[7] The first chelate laser was tetrakis Eu(III) benzoylacetonate in a methanol/ethanol glass at -150°C excited by a Xe flash lamp.[10] Studies on various β-diketone ligands in different solvents determined the best system for room temperature operation.[11] In 1964, laser emission at 611.8 nm (the ${}^5D_0 \rightarrow {}^7F_2$ transition) was obtained at room temperature from tetrakis Eu(III) benzoyltrifluoroacetonate in acetonitrile.[12] The chelate lasers have high threshold energies and low output energies, so they have not been used commercially.[13] However, there has been a great deal of information learned about energy transfer processes from deuteration, solvent and substitution effect studies with the chelate systems.[14]

Nd(III)-Aprotic lasers

Nd(III) is the best performing ion in solid lasers, but has a luminescence quantum yield of 10^{-5} in aqueous solutions.[4] Deuteration studies showed that the quantum yield was dependent on the number of hydrogens in the ion's immediate environment.[15,16] Heller at Bell Labs chose $SeOCl_2$ as an aprotic solvent which also had the necessary high dielectric constant and transparency in the wavelength region of the pumping source. Lewis acids such as $SbCl_5$ or $SnCl_4$ were added to increase solubility and prevent self-quenching.[17] In 1966, Heller reported laser action at 1055.0 nm (the ${}^4F_{\frac{3}{2}} \rightarrow {}^4I_{\frac{11}{2}}$ transition) at room temperature from the Nd(III)-$SeOCl_2$-$SnCl_4$

system.[18] Nd(III) in the less toxic aprotic solvent solvent $POCl_3$ and added Lewis acid gives laser emission at 1051.0 nm with comparable performance parameters.[19,20] Heller also reported laser action from o-phenanthroline adducts of perhalo acid salts of Nd(III) dissolved in deuterated dimethyl sulfoxide, but the quantum yield was lower than for the Nd(III)-aprotic solvent system.[21]

The Nd(III)-based liquid lasers give much better performance than the chelate lasers and are in fact comparable to most pulsed solid state lasers.[22]

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A KINETIC STUDY OF AMINE SUBSTITUTIONS IN PENTA-CARBONYL(AMINE)MOLYBDENUM(0) COMPLEXES

(Thesis Report)

William D. Covey November 2, 1972

INTRODUCTION

Substitution and exchange reactions of transition-metal carbonyl complexes and their derivatives have been extensively researched in the past decade. Several reviews adequately cover all kinetic studies through 1967.[1] No attempt will be made here to cover in detail work accomplished since 1967. Rather, in the material that follows, attention will be focused on amine substitution on pentacarbonyl(amine)-molybdenum(0) complexes, $Mo(CO)_5$(amine), by Lewis bases. The reaction mechanism in this system is not well understood. The stoichiometric reaction is

$$Mo(CO)_5(\text{amine}) + L \rightarrow Mo(CO)_5(L) + \text{amine}. \qquad (1)$$

The rate law observed for this reaction has two terms.[2]

$$\text{Rate} = (k_1 + k_2[L])\,[Mo(CO)_5(\text{amine})]. \qquad (2)$$

The first-order term suggests prior dissociation of amine to form a five-coördinate intermediate, $Mo(CO)_5$, which then reacts with ligand to form product. The second-order term suggests direct displacement of amine by reagent ligand. The proposed mechanism is as follows, using 'M' to symbolize the $Mo(CO)_5$ moiety, 'A' the amine, and 'L' the reagent ligand,

$$MA \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} M + A \qquad (3)$$

$$MA + L \xrightarrow{k_2} ML + A \qquad (4)$$

$$M + L \xrightarrow{k_{11}} ML \qquad (5)$$

There is spectroscopic evidence for formation of the proposed five-coördinate species from hexacarbonyl irradiated in matrices at low temperatures.[3] This five-coördinate species is also proposed as an intermediate in thermal carbonyl exchange[4] and substitution[5] on the hexacarbonyl complex.

There are *a priori* objections to the proposed direct displacement of amine by reagent ligand. This process would entail severe steric crowding with the formation of a seven-coördinate activated complex and attack by the reagent ligand at sites around the metal atom that are occupied by metal t_{2g} d-electrons.

Characterization of the kinetic behavior of the postulated five-coördinate intermediate and of the intimate details of the second-order process will aid in the elucidation of substitution reactions on this and other transition-metal carbonyl complexes.

The present study investigates the rates and mechanisms of amine substitution from $Mo(CO)_5$(amine) in detail as a function of amine, reagent ligand, solvent, and temperature. The results and conclusions are summarized in the next section.

RESULTS AND CONCLUSIONS

Activation parameters for reaction of PPh_3 with $Mo(CO)_5$(amine), where amine = cyclohexylamine, piperidine, and quinuclidine, in cyclohexane calculated from Arrhenius and Eyring plots support the proposed two-pathway mechanism. The parameters are significantly different for the two processes with almost a 2-fold change between the enthalpies of activation. The lower enthalpy and a quite negative entropy of activation support the direct displacement mechanism proposed for the second-order process.

The first-order rate for reaction of PPh_3 with $Mo(CO)_5$(amine) in hexane at 35° shows a 50-fold decrease with a change in amine from cyclohexylamine to quinuclidine. The rate is an orderly function of amine basic and steric characters. The facts support a dissociative mechanism for this process.

The second-order rate for reaction with $Mo(CO)_5$(piperidine) in hexane at 35° shows only slight sensitivity to basic character of reagent ligand. There is scarcely a 10-fold increase in rate with a change in reagent ligand from $P(OPh)_3$ to $P(OCH_3)_3$. Indeed, ligand steric character is more determinative of reactivity than basic character. The facts indicate that bond-making is less important than bond-breaking in the transition state of this process.

The first- and second-order rates for reaction of PPh_3 with $Mo(CO)_5$(piperidine) at 35° are differently influenced by the nature of solvent. A 3-fold increase in the first-order and a concurrent 30-fold decrease in the second-order rates occur with a change in solvent from hexane to nitromethane. There is evidence for direct displacement of amine by very basic solvents. Hydrogen-bonding is excluded as a rate enhancing factor on the basis that no acceleration occurs with a change in amine from cyclohexylamine to piperidine to quinuclidine. The decrease in the second-order rate is rationalized on the basis of greater solvation of the substrate by basic solvents.

Competition ratios, (k_{-1}/k_{1}), were obtained for reaction of $Mo(CO)_5$(piperidine) in hexane at 35° with PPh_3, $AsPh_3$, and $P(OCH_3)_3$. The ratios were all essentially unity and indicate indiscriminate reactivity of the five-coördinate intermediate.

The data suggests that the substitution mechanism is perhaps best described as an interchange mechanism, or more specifically 'I_d' in the nomenclature of Langford and Gray.[6]

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GAS PHASE THERMODYNAMIC AND KINETIC MEASUREMENTS: APPLICATIONS TO IONIC CLUSTERING EQUILIBRIA

Tony J. Beugelsdijk 9 November 1972

The interactions of ions with solvent molecules has been studied for many years in liquid solutions. Of recent interest[1-8] has been a new approach, namely, the study of ion-solvent interactions in the gas phase. This method has the special advantage of studying ion-molecule complexes without the interference of the bulk of the solvent. These studies are thus specially suited to provide information concerning the interactions between the central ion and solvent molecules in the complete or incomplete first and second solvation shells.[9,10]

One example of such an equilibrium is the clustering of water molecules around an alkali ion, M^+, i.e.,

$$M^+(H_2O)_{n-1} + H_2O = M^+(H_2O)_n \qquad (n-1,n)$$

Information obtained on the hydration equilibria for the alkali ions furthers the understanding of many related gas phase systems such as those observed in the D-region of the ionosphere,[11] in flames,[12] and in mobility experiments.[13]

The experimental method relies upon the mass spectrometric determination of the intensities of the reactant ions escaping through a small leak from a reaction chamber containing a known pressure of solvent vapor. Thermodynamic quantities are then obtained from the calculated equilibrium constant and its temperature dependence.[14,15]

A major source of controversy with reference to the fundamental assumption of the achievement of equilibrium has arisen in the literature.[16] Beggs and Field have made an extensive effort to determine the effects of the instrumental parameters upon the ion intensities and equilibria in the system. They found that only the repeller and the ion-accelerating potentials affected the equilibrium constants in any way. With the appropriate corrections their results agree with their earlier work and that of Kebarle for n = 3, 4, and 5. The dispute continues as a result of discrepancies in the data for n = 1 and 2.[17,18]

Further questions regarding equilibria have led to kinetic measurements for bi- and termolecular association of the hydrates. Heretofore only a narrow range of pressures and temperatures at which the establishment of equilibrium was assumed to be fast (not requiring a longer time than about 100 microseconds) was used. All previous calculations showed a considerable degree of internal consistency and were believed to be reliable, but it remained necessary to establish proper confidence limits. The high-pressure pulsed quadrupole mass spectrometer used by

Kebarle[19,20,21] is uniquely suited to obtain data in high-pressure regions. Pressure up to 10 Torr can be used and the ion reaction times can be as long as several hundred microseconds. The system is specially adaptable for studying reactions with very small rate constants, long reaction sequences, and reactions in which third-body collisional stabilization plays an important part in changing the nature of the reaction products. In the case of reversible reactions, the establishment of equilibrium can be directly observed.

Mechanisms and rate constants of the ion-molecule reactions leading to the formation of $H^+(H_2O)_n$ in moist oxygen, nitrogen, and air were determined. The clustering reactions were found to be third order for $n = 1$ to $n = 4$ consistent with a third-body collisional stablization mechanism. Comparable values were obtained by the flowing afterglow technique[22,23] developed by Ferguson.[24]

Since the alkali and halide ions are spherical, one might expect that their hydration energies should be most amenable to classical calculations based on ion-dipole interactions. Despite the well-known electrostatic representation of closed shell ion-neutral bonding, bond energies have not been thoroughly explained; not even for one water molecule bonded to an ion. The difficulty has been in knowing exactly the repulsive interactions. Spears[25] proposes and defends a two-parameter repulsive term as opposed to the classical one-paramenter "hard core" formalism. Contrary to previous estimates on halide systems, he finds little contribution from the ion-quadrupole energy and insignificant covalence in the bonding of the clusters.[26]

Extensions of this work, now in progress, include clustering to small charged radicals (i.e., OH^-, O_2^-, NO^-)[27] and dipositive ions (i.e., Ba^{2+}, Mg^{2+}).[28] Solvation effects in proceeding from protic solvents such as water and methanol to aprotic solvents such as acetonitrile and carbon monoxide have lately been described.[29] Mathematical models to fit experimental data[30] and a more extensive description of the bonding would prove valuable.

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ORGANOCOBALT CHEMISTRY

Jan Collard November 14, 1972

Inorganic chemists have become interested in many biochemical systems containing transition metals. One of the most studied systems is coenzyme B_{12};[1] which has many important functions in the body. Coenzyme B_{12} is a six coordinated cobalt(III) complex with a strong field in-plane corrin ligand. The upper axial position is occupied by an adenosyl group attached covalently through the 5' carbon atom, and the lower axial position is occupied by a nitrogen atom of 5,6 dimethylbenzimidazole. The presence or absence of the benzimidazole changes the kinetic reactivity and oxidation-reduction potential of the cobalt center without qualitatively changing the chemical character of the coenzyme.

Vitamin B_{12} has essentially the same structure as coenzyme B_{12} with the exception that the upper axial ligand has been replaced by CN^-, OH^-, or other anion. If the lower axial ligand is the benzimidazole, the series of complexes is called cobalamins, while if the benzimidazole nucleotide has been removed and replaced by another base, the series is referred to as cobinamides.

Many model systems have been synthesized which duplicate the chemical and electronic environment around the cobalt ion in the B_{12} system. Chief among these are the cobaloxime compounds, first studied by Schrauzer.[2] The upper axial position may be occupied by an anion or alkyl group, while the lower axial position may be occupied by a coordinating ligand such as amine, phosphine, etc.

The important reactions of the B_{12} system are hydrogen transfer and methyl transfer. Methyl transfer may proceed by three different routes: (1) heterolytic cleavage to yield a cobalt(III) complex and methyl anion, (2) homolytic cleavage to give a cobalt(II) complex and methyl radical, (3) a heterolytic cleavage yielding a cobalt(I) complex and methyl carbonium ion. The evidence accumulated thus far indicates that the cobalt-carbon bond is cleaved heterolytically to yield an electrophilic organic moiety and the powerfully nucleophilic cobalt(I) complex.

It has been shown that the axial ligands profoundly affect the reactivity of these compounds. The polarographic behavior of the cobalamins was investigated by Hogenkamp and Holmes.[3] They studied the dependence of the first reduction potential on the upper axial ligand. They also investigated the polarographic behavior of the cobinamides and found them to be dependent on both axial ligands. Schrauzer[4,5] investigated the polarographic characteristics of the cobaloximes and compared them to the characteristics of vitamin B_{12}. Hohokabe[6] correlated the first half-wave potential of the cobaloximes with the charge transfer transition energies. Both found the electrochemical behavior of these complexes to be somewhat dependent on the axial ligands coordinated to the cobalt.

Because the cobalt(I) moiety of coenzyme B_{12} may be a very important intermediate, the reduced forms of the coenzyme and of the model compounds have been extensively investigated. Schrauzer[7] compared nucleophilic reactivities among several complexes. If the nucleophilicity is defined as $nCH_3I = \log(k_Y/k_{CH_3OH})$[8] where k_Y and k_{CH_3OH} are respectively the second order rate constant for attack by a nucleophile Y and methanol on the substrate CH_3I at 25° in methanol as the solvent, he found a dependence of the nucleophilicity on the lower axial base and the in-plane ligand.

Because the cobalt(I) complexes are strongly nucleophilic, they react with alkylating agents. There is a correlation[9] between the alkylation rates and the nucleophilicities of the cobalt(I) moieties. Alkylation is reported to follow second order kinetics and to occur via a classical S_N2 mechanism. By studying the β elimination reactions of the alkylcobaloximes,[10] Schrauzer demonstrated that the initial product is the π complex of the cobalt(I) nucleophile. The π complex is in equilibrium with the free cobaloxime(I) nucleophile and the olefinic elimination product. π complexes of vitamin B_{12} were found to form π complexes only upon addition of strong π acceptors to aqueous-alkaline solutions of the vitamin. Although a π complex of B_{12s} has not yet been observed, it is postulated that such a mechanism is possible.[11]

It is essential that the properties of vitamin B_{12} be understood before the enzyme reactions in which it acts as a coenzyme can be understood. Studies on simple model systems help to elucidate these properties and also lead to interestingly new ideas.

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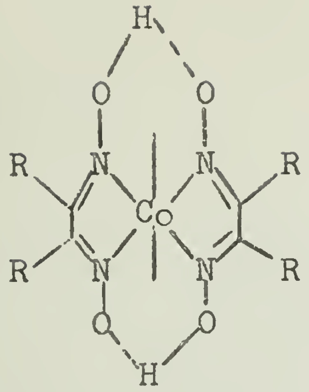
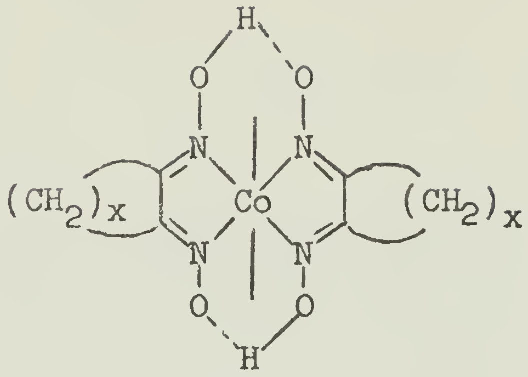
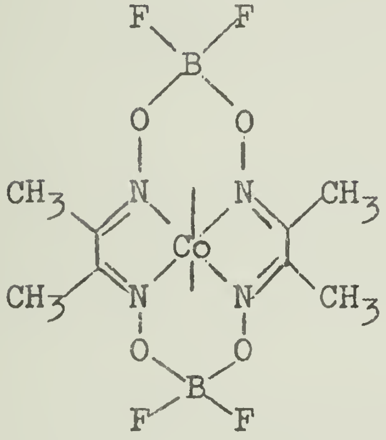


I, R=CH_3
II, R=C_6H_5
III, R=H



IV, x=4
V, x=3



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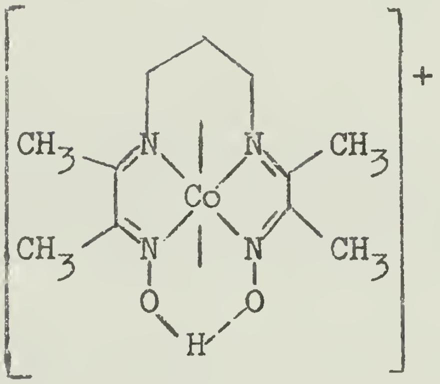
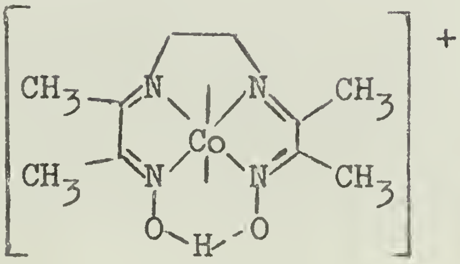


VII



VIII

MODEL SYSTEMS FOR FERREDOXINS

Gerald Delker November 21, 1972

Introduction

The iron-sulfur proteins known as Ferredoxins are important in many biological systems which involve the transfer of electrons.[1,2] Many different iron-sulfur compounds have been synthesized in an attempt to duplicate the electronic and physical characteristics of Ferredoxins. Several model systems have been found which approximate the electronic spectra and have helped to clarify the structure of the iron-sulfur group in the different Ferredoxins.

Ferredoxins

Ferredoxins are a class of electron transfer proteins important in photosynthesis, nitrogen fixation, and in the metabolism of bacteria, plants and animals.[3] All Ferredoxins have three characteristics in common: all contain the acid-labile sulfide (S*) in equimolar ratio to iron; all show reduction potentials in the range from -240 to 420 mV; and when reduced, all display an uncommon E.S.R. signal with an average g-value of about 1.94.[4]

Model Systems

Ferredoxins can be divided into two basic types: 2Fe-2S* and 4Fe-4S*.[5] On this basis, the iron-sulfur compounds can be considered as either dimers or as clusters of iron and sulfur. The dimeric compounds studied can be further divided into organosulfur and sulfide bridged compounds.

The organosulfur bridged compounds were the first type investigated. Most of the early work was done with carbonyl[6] and nitrosyl[7] iron compounds bridged with thioethyl and thiophenyl, but these compounds are not satisfactory models. The compound $[Fe(C_5H_5)(CO)(SC_2H_5)]_2^+$ has been found to have an average g-value just less than the free electron value, as is the case with reduced Ferredoxins, but the anisotropy is different.[8] Other organosulfur bridged compounds such as $[Fe_2(SCRCRS)_4]^z$, z = 0, +1, +2, have also been studied.[9,10] However, these are not likely models for Ferredoxins since the sulfur is not labile.

The sulfide bridged iron compounds are more consistent with the biochemists' ideas on the nature of the iron-sulfur structure. Model systems like $[Fe_2S_2(SCRCRS)_2]$[11] tend to duplicate the suggested structure of 2Fe-2S* Ferrodoxins. Little advanced study has been done with model dimeric compounds with sulfide bridges since spectroscopic studies on the 2Fe-2S* Ferredoxins have revealed sufficient information to interpret the iron-sulfur structure.[2,12-14]

Most work on model systems for Ferredoxins has been concerned with the 4Fe-4S* compounds. $[Fe(C_5H_5)S]_4$, synthesized in 1965, is a cluster compound with the iron atoms at the corners of a tetrahedron and the sulfide atoms above the faces.[15,16] A similar configuration is also found for $[Fe_4S_4(SCRCRS)_4]^{2}$ [17,18] and $[Fe_4S_4(SCH_2C_6H_5)_4]^{-2}$.[19] The latter compounds have physical and electronic properties comparable to the 4Fe-4S* Ferrodoxins. An x-ray study of Ferredoxin at 2.5 Å resolution supports the cluster arrangement or iron and sulfur.[20]

Unresolved Questions

Recent work has presented new problems, including evidence that a S-S bond might exist in Ferredoxin,[21] and that the iron atoms do not necessarily exist in identical environments.[18] Still unresolved is the structure of the 8Fe-8S* bacteria Ferredoxins, though they are thought to consist of two 4Fe-4S* clusters. The iron-sulfur protein HiPIP, which is a 4Fe-4S* protein, is similar to 4Fe-4S* Ferredoxins, however, its redox potential is unexplainably different. Also, the method of electron transfer in the biological systems is still uncertain.

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PATTERN RECOGNITION: CHEMICAL APPLICATIONS

Robert Kabler November 28, 1972

Pattern recognition,[1-3] a subset of the broad discipline of artificial intelligence, has been successfully applied to such diverse problems as fingerprint analysis, speech analysis, handwritten and printed alphanumeric character recognition, taxonomic classification and many others for more than a decade. In the past few years, one particular pattern recognition method, the linear learning machine,[4] has been applied to various types of spectroscopic data. The goal of pattern recognition is to predict particular properties of substances from a large amount of seemingly unrelated data.

Pattern recognition can be divided into two categories: parametric and nonparametric. Parametric methods require that the probability distribution functions of the classes are known or can be estimated. These aren't known for most chemical problems so parametric methods are of little use to the chemist. Preprocessing consists in numerically operating on data in order to change the representation of information contained. Preprocessing may amount to no more than scaling the measurements, but often includes transformations such as autocorrelation[5,6] and Fourier.[7] In supervised learning, training is undergone to develop a rule which will correctly predict to which class a series of labeled points belong. The rule is then applied to unknown points to determine their classifications. Unsupervised learning involves finding realistic clusters of points in n space which reflect the existence of meaningful relationships. The data may be multi-source, i.e., measurements coming from a variety of instruments, or single-source. A digitized spectrum is a good example of single-source data. Almost all of the early applications of linear learning machines to mass,[7-14] infrared,[15] nuclear magnetic resonance,[5] and gamma ray[16] spectroscopy have been to single-source data. One attempt was made to combine IR and mass spectral data.[17]

Learning machines[4] operate by dichotomizing n space with a decision surface. For linear learning machines, this decision surface is called a hyperplane. All points that fall on one side of the hyperplane belong to one class and all points that fall on the other side of the hyperplane belong to the second class. The side of the hyperplane that a point falls on is determined by the sign of the dot product of the n+l dimensional weight vector, which determines the orientation of the hyperplane, with the augmented pattern vector. Training is normally an iterative feedback process where each known spectrum is tried. If the wrong classification results, then the weight vector is corrected by adding to it a fraction of the augmented pattern vector. This proceeds until all of the training set have been correctly classified. If training can not be completed, then either the classes are not linearly separable or the data are in the wrong form.

This method was used with a great deal of success in the area of mass spectrometry. The early work[8-10,14] was just molecular formula determination, but the later work[7,11-13] included the determination of types as well as the number of functional group of each type. Shortcomings in this method became very evident in the first application to nmr.[5] The difficulty lies in the fact that there are a great many hyperplanes which will recognize the training set properly, but will give varied predictions for the unknowns. The particular hyperplane obtained is a function of the ordering of the training set as well as the correction increment used. This fact has caused some workers to use two hyperplanes to define the empty region between two classes. This, however, can lead to no decision areas which is probably no better than a possibly incorrect classification. Another problem with learning machines is that there is no theory available which gives error limits for the classification made.

Kowalski and Bender, in a recent paper[6] on pattern recognition applied to nmr, have suggested the use of the K nearest neighbor classification rule,[18] Knn, as an alternative to the learning machine classification technique. Knn has been heavily treated theoretically,[19,20] so a great deal is known of its properties. The classification of an unknown is determined by the majority rule of its K nearest neighbors. Knn gave substantially better results than the learning machine and does it cheaper for no training is necessary.

All of the learning machine applications have been supervised learning. There are a large number of clustering algorithms available for unsupervised learning.[21,22] Kowalski and Bender recently published a paper[23] in which they attempted to use a clustering algorithm to group elements according to whether the oxide of the element was acidic or basic. A technique called non-linear mapping[24] is used to map the clusters obtained from the six dimensions used down to two, thus allowing visual inspection. Although the clusters are not well resolved, a separation is obtained. The Knn was used to classify those oxides normally considered to be amphoteric with good success.

Pattern recognition will be of greater value once a number of different programs become accessible to the chemist. Work is needed to determine what types of algorithms are best for a particular type of problem to allow the non-specialist to use the techniques in much the same way that many chemists use molecular orbital programs. I can foresee chemists using pattern recognition to avoid research in areas of low success probability in a manner similar to that employed by Nakagawa,[25] in the area of phenazine production in Pseudomonads.

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CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION

Robert G. Mayer December 5, 1972

Introduction

In 1967, J. Bargon, H. Fisher, and U. Johnsen noticed an NMR emission line for benzene during the thermal decomposition of benzoyl peroxide in cyclohexanone.[1] Other reactions run in NMR spectrometers showed such emissions and, sometimes, enhanced absorption. In all cases, this phenomenon occurred in the lines assigned to product compounds and the reactions were known to have, or could be postulated to have, radical intermediates. The original explanation[2,3] for the phenomenon involved cross polarization of nuclei in the radicals by the unpaired electrons in a manner analogous to the Overhauser Effect, hence the name Chemically Induced Dynamic Nuclear Polarization (CIDNP). The Overhauser Effect could not explain[4] enhancements greater than a factor of 128, nor the so-called multiplet effect. The radical pair theory was proposed[5,6] which assumed that the spin states of "caged" radical pairs are coupled and that the rate of combination of this pair is proportional to its singlet character. The singlet character of this pair is nuclear spin state dependent, yielding products with non-equilibrium nuclear spin states. The theory has been expanded to account for the diffusive motion of the radicals forming pairs[7] and has been refined and put on a firm quantum-mechanical and kinetic basis.[8]

Radical Pair Theory

The present theory of CIDNP depends on spin interactions and reaction rates of radical pairs. The theory has been reviewed,[4,9,10,11] and has been developed most thoroughly by Kaptein.[8,12] The magnitude and the sign of the enhancement of product NMR signals depend on the manner of formation of the radical pair. The radical pair may be formed in a singlet state (type S formation), generally thermally or from a photochemically generated singlet state; it may be formed in a triplet state (type T formation), generally from a photochemically generated triplet state, or the radical pair may be formed by a random encounter of radicals (type F formation) in which one would expect an equal population of S, T_{-1}, T_0, and T_1 states.

The two coupled electrons in the radical pair precess in the spectrometer's magnetic field. The singlet state is that in which the two electrons are aligned oppositely in the field and are precessing 180° out of phase with one another; the triplet (T_0) state is that in which the electrons are aligned oppositely in the field but are precessing in phase with one another. The rate of precession of one of the electrons (ω_s) is given by

$$\omega_s = \theta\hbar^{-1}[gH_0 + \Sigma a_i m_i]$$

(g is the g value for the unpaired electron in the radical and a_i is the hyperfine splitting constant for nucleus i with spin state m_i). Since a phase change of 180° by one electron with respect to the other will change a pure S state to a pure T_0 state and vice versa, the rate of S-T_0 mixing, δ, depends on the difference in precession

rates of the two electrons.[4]

$$(\omega_{S_1}-\omega_{S_2}) = 2\delta = \beta\hbar^{-1}[(g_1-g_2)H_o + (\Sigma a_{1_i}m_{1_i}-\Sigma a_{2_j}m_{2_j})]$$

The rate of S-T_o mixing is nuclear spin state dependent and S-T_o mixing will occur even with chemically identical radicals if the nuclear spin states of the radicals differ. This development has assumed that J, the electron exchange integral for the two radical electrons, is negligible.

Radicals in radical pairs can react in one of two ways: they can form "cage" products from the radical pair (type P products) or they can fail to react with each other and form "escape products (type D products). The probability of type P reaction of a radical pair is directly proportional to its singlet character (assuming a singlet product). So, for instance, if one has type T formation of radical pairs, type P ("cage") products will form preferentially from radical pairs with a greater δ which means that the product will have a non-equilibrium nuclear spin state.

The multiplet effect is a phenomenon which shows both emission and enhanced absorption in a multiplet of magnetically equivalent nuclei. Multiplet effects may be classified as A/E or E/A, depending on the relationship of the absorption and emission peaks with increasing field strength. Formulae for determining the direction of enhancement and the type of multiplet have been derived.[13]

This simplified theory of CIDNP may be extended[6] by including J, by considering the role of diffusion[14] on radical reactions,[7] and by full consideration of the kinetics involved.[8,12]

Applications

CIDNP may be used[10] to give evidence for radical intermediates where other methods may fail; it enables studies of mechanistic pathways; it may show the spin state of the radical pair precursor, giving information about the spin state of a photochemical intermediate; the phenomenon may occur in reactions in which the reactants and products are the same, showing that reaction occurs. Finally, it may yield information about physical properties such as g values, nuclear hyperfine constants, and nuclear relaxation times. CIDNP has been used to study[10] photochemical or thermal reactions of various organic peroxides, aldehydes, ketones, and carbenes. It has also been used to study alkyllithium-alkyl halide reactions.[15,16]

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METALLOCARBORANES

Dennis Sekutowski December 19, 1972

Throughout the early days of boron hydride chemistry, very little was known with respect to their structures. They were regarded as unstable and highly reactive chemical oddities. Elucidation of their structures made it necessary to devise new approaches to a theory of chemical bonding. Further studies and research lead to the discovery of the extraordinarily stable polyhedral borane ions and the isosahedral $B_{10}C_2H_{12}$ carboranes. In 1965, M. F. Hawthorne successfully performed the marriage of these carboranes to transition metals, thus opening up a new field for the coordination chemist.

1,2-Dicarba-closo-dodecarborane(12), $B_{10}C_2H_{12}$, first began appearing in the literature in the early 60's.[1] It was found that a strong base could selectively degrade the molecule to give $(1,2\text{-}C_2B_9H_{12})^-$. Removal of a proton lead to 1,2-dicarbollide, which has a five-member edge ring containing six electrons and having molecular orbitals analogous to the cyclopentadienide ion, $C_5H_5^-$. Reaction of this ligand, under similar anhydrous conditions used in the initial preparation of ferrocene, lead to the first metallocarborane. Attempts to make a mixed ligand system resulted in isolation of the neutral compound: (C_5H_5)-Fe$(1,2\text{-}B_9C_2H_{11})$.[2,3] A. Zalkin, D. Templeton, and T. Hopkins proved by doing the crystal structure, that, indeed, it has the "sandwich" structure and that the metal is equidistant between the ligands.

In the few years since this preparation, over one hundred metallocarboranes have been synthesized, using most of the transition metals in a wide variety of oxidation states.[4,5,6] The visible spectra, magnetic susceptibilities, NQR's, and ESR's of most of these complexes are all very similar to the analogous metallocenes. The metallocarboranes, however, have greater thermal and chemical stability and favor the higher oxidation states of the metals.

An example is the $[(C_6H_5)_3PCH_3]Cu(1,2\text{-}B_9C_2H_{11})_2$ system.[7] Cu(III) is relatively unheard of in organometallic chemistry. R. W. Wing's crystal structure of this compound showed that it has a "slipped" structure; i.e., the metal is shifted about 0.6 Å from the center of the carborane rings with the M-C distance greater than the M-B distances. This "slipped" structure has appeared in all crystal structures of electron rich d^8 and d^9 metallocarboranes.

Attempts to prepare metal-σ bonded carboranes succeeded when using biscarborane as the ligand with Ni, Co, Cu, and Zn metals.[8] These appear to be chelation reactions which work for these electron rich metals. These compounds were assumed to have either pseudo square-planar or tetrahedral symmetry around the metal. R. A. Love and R. Bau have recently completed a crystal structure of one of these cobalt complexes, proving that the bonding is a bit more complex than suspected, since they have found evidence for a B-H-M bond, giving a structure that they describe as a "badly distorted square pyramid."

Further research showed that chelation reactions were not necessary to form stable σ-bonded carboranes, as the $(B_{10}C_2H_{11})$-ligand was incorporated in stable neutral iron(II) and manganese(I) carborane complexes.[10] In fact, the number and complexity of these σ-bonded derivatives may surpass in the future those of the corresponding π-bonded derivatives.

One added note is that carboranes, like many other aspects of inorganic chemistry, are beginning to be important biochemically, specifically, in cancer therapy.[11] This is based on the unique nuclear property of the ^{10}B nucleus to absorb thermal neutrons and the ease of incorporating carboranes into antibody proteins specific to human histocompatibility antigens.

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THE PHOTOCHEMISTRY OF CHROMIUM(III) COMPLEXES

Ben Tovrog

January 9, 1973

Introduction

Chromium(III) photochemistry has been studied widely and in great detail. From large amounts of direct photochemical data, two different mechanisms have been proposed to explain observed photoreactions. This seminar will briefly discuss these two mechanisms and recent work in sensitized photochemistry which have helped resolve this mechanistic question.

Spectroscopy of d^3 Systems

In the presence of a strong octahedral field, the ground state of a chromium(III) complex has a $t_{2g}{}^3$ configuration; the first two excited states are $t_{2g}{}^2e_g$ and $t_{2g}e_g{}^2$. Of importance in photochemistry and luminescence is the nature of the ground state $^4A_{2g}$ and the lowest lying excited states of various spin multiplicity: ^2E_g, $^4T_{2g}$ and $^4T_{1g}$. For octahedral complexes, transitions from $^4A_{2g}$ to all these excited states can be seen in absorption, while frequently only the $^2E_g \rightarrow {}^4A_{2g}$ transition is seen in emission.[1]

The ^2E_g state and $^4A_{2g}$ ground state arise from the $t_{2g}{}^3$ strong field configuration, consequently their bonding is very similar and little excited state distortion exists. Absorption and emission (phosphorescence) show very small Stokes shift and vibrational fine structure is often seen in the spectra. The $^4T_{2g}$ state arises from the $t_{2g}{}^2e_g$ configuration; when fluorescence is observed, it is subject to large Stokes shifts, the bands broad and structureless. Whether phosphorescence, fluorescence or both are observed is dependent on the average ligand field strength, the $^4T_{2g}$ energy increasing with Δ, ^2E remaining independent of Δ.[2,3]

Photochemistry of Octahedral Complexes

The vast majority of chromium(III) complexes studied undergo photosubstitution of solvent as their main photochemical reaction. The quantum yields tend to be wavelength independent over the ligand field absorption region with very small temperature dependences.[4] Luminescence data indicate the lifetime of ^2E_g is about 10^{-3} seconds, the lifetime of $^4T_{2g}$ about 10^{-7} seconds. These facts led Schlafer[5] to believe the ^2E_g state played the most important role in the photochemistry, the longer lifetime of ^2E_g more favorable for approach of a substituting molecule. Also, the ^2E_g state can be indirectly populated by excitation of the upper quartet states which deactivate quickly to $^4T_{2g}$ and ^2E_g.

Photochemistry of Non-Octahedral Complexes

Though the doublet mechanism successfully explains photochemistry of octahedral complexes, it fails to explain that of non-octahedral complexes. In these complexes, two types of ligands are present, either of which may aquate, and cis-trans isomerization may occur.

Many data have been accumulated where two photoreactions for the same complex do occur, the ratio of their quantum yields wavelength dependent. This indicates that excitation to different excited states can lead to intermediates that are differently disposed to chemical reaction. Adamson believes these intermediates to be the excited quartet states. The main points of Adamson's theory are 1) in most cases, the $^4T_{2g}$ state lies below the ^2E_g state and 2) the lifetime of the $^4T_{2g}$ state may be as long as 10^{-6} seconds, which is the half-life needed for a unimolecular reaction with an activation energy of 10 kcal.[6]

Energy Transfer

Electronic energy transfer processes between organic molecules have been extensively studied,[7] recently organic molecules with long-lived triplet states have been used to sensitize emission and photoreactions in chromium(III) complexes.

Adamson and co-workers have studied the direct and sensitized photochemistry of $Cr(NH_3)_5(NCS)^{2+}$. Both ammonia and thiocyanate aquation occur, the quantum yield ratio $\emptyset NH_3/\emptyset NCS = 22.2$ and 8.3 for direct excitation in the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^2E_g$ bands respectively. These observations are consistent with $^4T_{2g}$ responsible for ammonia aquation, ^2E_g for thiocyanate aquation.[8] These results are in agreement with the sensitized photoreactions. Energy transfer from the biacetyl triplet and the acridinium ion singlet states populate the quartet state of the complex resulting in 100% and 97% ammonia aquation respectively, in comparison to 95.5% for direct excitation. The acridinium ion triplet state populates the doublet state of the complex and results in 100% thiocyanate aquation. These results also indicate the quartet state of the complex undergoes only ammonia aquation, the small thiocyanate component reflects varying degrees of intersystem crossing to the doublet state, which is responsible for only thiocyanate aquation.[9,10]

Porter and co-workers[11,12,13] have studied intermolecular energy transfer between two chromium(III) complexes as a means of exploring the details of photochemical reaction. The quenching of $Cr(NH_3)_2(NCS)_4{}^{2+}$ (reinekate ion) phosphorescence by $Cr(CN)_6{}^{3-}$ left one-half of the reinekate ion aquation unquenched. This indicates the doublet/doublet character of energy transfer, and that at least one-half of the photoreaction must originate from the quartet state before reaching the doublet state. Similar results where phosphorescence could be totally quenched while the photoreaction could not have been observed for $Cr(phen)_3{}^{3+}$ [14] and $Cr(NH_3)_6{}^{3+}$.[15]

In most chromium(III) complexes, thermal repopulation of the $^4T_{2g}$ after population of the ^2E_g state is possible, and can lead to photoreaction. When such a process occurs, it is difficult to distinguish which excited state is the precursor to reaction. To decide between the two possibilities, $Cr(CN)_6{}^{3-}$ was studied as this complex has the largest known energy separation between $^4T_{2g}$ and ^2E_g. A thermal equilibrium between the two states is therefore improbable. It was observed that 1) phosphorescence could be sensitized by energy transfer from anthracene, 2) no sensitized photoreaction could be obtained and

3) phosphorescence is strongly quenched by water, or by O_2 dissolved in DMF, but the photochemical quantum yields differ little in water or DMF. These differences rule out the possibility that the photoreaction and the phosphorescence originate from the same excited level. As the phosphorescence originates from the ^2E_g state, the photoactive state must be $^4T_{2g}$.[16]

Conclusion

A definite problem with conventional ligand field theory exists in the case of chromium(III) complexes in that one cannot predict theoretically the energy and geometry of excited states. For the present, emission and photochemistry are providing some indirect evidence as to their nature, however, a modification of ligand field theory to include excited states would be most useful.[17,18]

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TRANSITION METAL CARBENE COMPLEXES-

THE NATURE OF THE CARBENE LIGAND

Frank S. Wagner March 6, 1973

Introduction

The first transition metal carbene complexes were prepared over fifty years ago,[1] although their structure and bonding were not understood until recently.[2] Pioneering work by E. O. Fischer and co-workers has led to an avalanche of investigation into carbene complexes. To date, literally hundreds of carbene complexes have been prepared with a majority of the transition metal elements.[3]

The purpose of this seminar is to focus on the nature of the carbene as a ligand, and to briefly outline preparative methods and reactions of transition metal carbene complexes.

Classification

The term "metal-carbene" refers to complexes of the type $(L)_nM-C(X)(Y)$ where $:C(X)(Y)$ is the carbene ligand, M the central metal, and L simply represents other ligands. In valence bond terminology, the carbene ligand may be considered to be sp^2 hybridized, although alkenyl-metal compounds, where the carbon atom is formally double bonded, are not included in the carbene classification.

Synthesis

Carbenes are synthesized by a variety of routes, the most versatile being the reaction of metal carbonyls with alkyllithium reagents. The resulting acylmetallate salt can be readily alkylated to give a carbene.[2] Other routes include reactions of isocyanide complexes with amines or alcohols,[4,5] or the reaction of salt-like precursors like sodium pentacarbonylchromate(II) with 1,2 diphenyl 3,3 dichlorocyclopropene.[6]

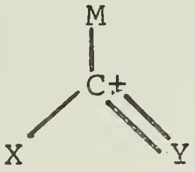
Reactions

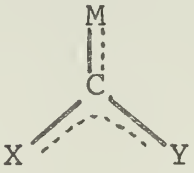
Transition metal carbenes undergo five major types of reactions which prove to be quite informative about the nature of the carbene ligand. The reactions are: L-substitution; carbene substitution: "ester" cleavage; reaction at the metal-carbene bond; and hydrogen abstraction.[7] Depending upon the substituents, an alkoxycarbene derivative such as $(CO)_5CrC(OMe)Ph$ is readily susceptible to amination by either a primary or a secondary amine, thus resembling the reaction of an organic ester.[8] The hydrogen atoms of an alkyl group attached alpha to a carbene carbon atom show an enhanced acidity, exchanging rapidly, when base catalyzed, in a methanol solution.[9] The carbon alpha to a carbene carbon atom is also readily alkylated.

Cleavage of a carbene ligand from a transition metal complex opens an extensive area of investigation. Either the free, highly reactive carbene, or the carbene complex itself can undergo a variety of reactions with suitable organic or inorganic substrates.[10]

Bonding

The coordinated carbene ligand can be represented with a variety of structures from limiting forms to a complete resonance system.





The vacant p_z orbital on the carbene carbon atom is able to π-bond with either X, Y, M, or any combination. For a typical carbene complex, $(CO)_5CrC(OMe)Ph$, x-ray data indicates that the M-C (carbene) distance is significantly longer than the M-CO distance.[11] This could indicate that the π-acceptor/σ-donor ratio is lower in the metal-C (carbene) bond. Much of the potential electrophilicity of the carbene carbon atom is relieved by π interaction with X and/or Y. Data on a variety of X and Y substituents indicate that the metal-C (carbene) bond is dependent upon the nature of X, Y, and L ligands coordinated to M.[10,12,13]

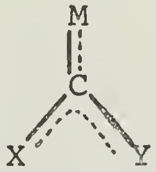
Infrared spectroscopy yields information about the charge transfer capabilities of the carbene ligand. Variation of the substituents X and Y markedly affect the CO stretching frequencies in complexes such as $(CO)_5CrC(OMe)Ph$.[7,10] Replacement of the alkoxy function with an amino group lowers the CO stretching frequency, indicating a decrease in the bond order of the CO ligand. The greater donor strength of the nitrogen atom reduces $d\pi$-$p\pi$ bonding between the carbene carbon atom and central metal, making available more electron density for the central metal.

The degree of "double bond" character in a carbene ligand can also be evaluated by the existence or non-existence of cis-trans isomers. The NMR spectrum of $(CO)_5CrC(CMe)(NMe_2)$ exhibits three distinct methyl resonances, confirming the barrier to rotation about the C(carbene)-N bond.[14] Fischer has carried out a detailed study on a series of $(CO)_5CrC(OMe)C_6H_4X$ complexes, where he considers the steric and electronic effects of various substituted phenyl groups on the stereochemistry of the carbene complex.[15]

Carbon 13 NMR indicates that the carbene carbon is shifted downfield relative to other carbon atoms in the molecule. In fact, the shift is comparable to a carbonium ion.[16]

Conclusion

The data presented seems to indicate that the carbene ligand is a good sigma donor while a weaker π-acceptor. The carbene carbon atom shows an electrophilic character as evident from C-13 NMR and chemical reactivity of the X and Y ligands. Both chemical and physical evidence confirm the strength of the M-C(carbene) bond and the varying contribution of $d_{\pi}-p_{\pi}$ bonding, depending upon the substituents. The carbene ligand can best be represented as a resonance structure with the limited forms possible depending upon the nature of the X, Y, L, and M ligands.



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SOME BIOINORGANIC ASPECTS OF MOLYBDENUM CHEMISTRY

Edward Denson April 12, 1973

Molybdenum has been shown to be an essential component of at least four enzyme systems: xanthine oxidase,[1] nitrate reductase,[2] aldehyde oxidase,[3] and nitrogenase.[4] The role of metals in complicated biological systems is often difficult to determine and inorganic models can provide a frame of reference for some systems, but are unnecessary for others. This seminar will concern itself with the role of molybdenum in xanthine oxidase, where models are not needed; and in nitrogenase, where models are sought.

XANTHINE OXIDASE

Xanthine oxidase is a high molecular weight (300,000) protein containing flavin, non-heme iron, labile sulfur, and molybdenum that catalyzes the oxidation of xanthine to uric acid and is important in the catabolism of purines. Electron spin resonance experiments[5] have greatly helped in elucidating the role of molybdenum as an electron carrier since an ESR signal typical for molybdenum(V) appears from the isotopically enriched enzyme in the presence of substrate. The complex spectrum consists of signals from at least two molybdenum environments, a free radical, and iron. Kinetic experiments using rapid freezing techniques have shown the order of appearance of the various signals, suggesting the order of electron transfer: Mo→FAD→Fe.[6] Experiments at 35 GHz[7] with deuterated substrate support the conclusion drawn from experiments at 9 GHz[8] that a proton from the C-8 position of xanthine is interacting with the molybdenum in the enzyme. Thus, molybdenum most likely interacts with the substrate and becomes reduced.

Less is known about the function of molybdenum in the other enzyme systems containing it and consequently model systems are of great use. All of the molybdenum enzymes, except purified nitrogenase, display similar ESR spectra. A survey of Mo(V) ESR spectra reveals that complexes containing the easily polarized ligands RS- and CN^- are the most similar to the enzymes in that they have small hyperfine constants (A) and high g values.[9,10,11] This is significant because of the high sulfur content of the molybdenum enzymes and points to sulfur containing ligands at the site of metal binding to the protein. People developing relevant model systems for these enzymes should keep this in mind.

NITROGENASE

Bacterial nitrogenase is a complex system requiring two proteins, one containing iron and molybdenum, and the other only iron; ATP; and a reducing agent ($Na_2S_2O_4$ is an adequate substitute for the natural reducing agent) catalyzing the reduction of molecular dinitrogen to ammonia. Other substrates of less importance containing triple bonds are also reduced (azide, N_2O, acetylene, nitriles, isonitriles, and HCN).[12,13,14] Unfortunately, the most purified extracts do not display an ESR signal and little has been learned about the function of

molybdenum from work with the enzyme itself. Consequently, model systems catalyzing the same reactions in aqueous solution, at ambient pressure and temperature, and using mild reducing agents, and inorganic complexes containing dinitrogen which may mimic the binding site in the enzyme, have been developed.

Schrauzer has developed a model consisting of MoO_4^{-2}, cysteine, ATP, $NaBH_4$ or $Na_2S_2O_4$, and traces of Fe^{+2} that mimics the enzyme in that it reduces acetylene,[15] isonitriles,[16] and nitriles,[17] somewhat less efficiently than the natural systems, but fails to produce more than trace amounts of $^{15}NH_3$ from $^{15}N_2$.[17] Nevertheless, a mechanism is proposed for acetylene reduction in which Mo(IV) is the substrate binding site and ATP functions in promoting solvolysis of the hydroxyl coordinated Mo(V) monomers to yield the active species.[15] It is then proposed that molybdenum is the active substrate binding site in the enzyme and that iron sites are associated with electron donors. However, since production of HD from D_2 and H_2O or H_2 and D_2O by active extracts of Azotobacter Vinelandii only occurs with dinitrogen as substrate,[18] and since it is obvious that a vital component necessary for N_2 reduction is missing from the model, exclusion of iron from the substrate binding complex based on the acetylene model is unwarranted. Moreover, Hill and Richards[19] have found that some other inorganic model systems containing thiol ligands reduce $^{15}N_2$ to $^{15}NH_3$ at greater rates than the Mo(V)-cysteine system, but only in the presence of both iron and molybdenum salts.

Dinitrogen complexes of transition metals are now well known and, since it is probable that iron and/or molybdenum function at the substrate binding site in the active enzyme, these complexes are relevant. Two types of complexes are the most common: terminal end-on bonded and linear bridged. Reduction of the $v(N_2)$ stretching vibration in the complexes points to weakening of the dinitrogen triple bond.[20] Rhenium(I) complexes have been studied the most and are useful models since they have the same number of d electrons as Iron(II). The lowest $v(N_2)$ has been found in a bridged complex of Re(I) with $MoCl_4$ as electron acceptor.[21] An approximate molecular orbital diagram for the π electrons in one of these linear bridged molecules (C_4v) shows that any acceptor having more than two d electrons will cause the dinitrogen bond to strengthen with respect to the terminal end-on bonded complex since the electrons will go into a 3e bonding orbital.[22,23] Also, any attempt to reduce these complexes will first cause the bond to strengthen for the same reason. Reduction has not been successful with reagents capable of existing in water. If the symmetry of the π orbitals could be reduced from C_4 to C_2, then the molecule would be similar to azobenzene in its π orbitals and more easily reduced.[20] Synthesis of model complexes of reduced symmetry having N_2 bridging between Fe(II) and Mo(IV) or Mo(V) may be an important step in the clarification of the active site of nitrogenase.

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THE DYNAMIC JAHN-TELLER EFFECT

Robert Richman April 24, 1973

In 1937 Jahn and Teller[1] showed that an orbitally degenerate state in any non-linear molecule is unstable with respect to a distortion which removes that degeneracy. In other words, when the electronic potential energy V is expanded in terms of normal coordinates Q about a symmetric nuclear configuration

$$V = V_0 + \sum_k \left(\frac{\partial V}{\partial Q_k}\right)_0 Q_k + \frac{1}{2}\sum_k \sum_l \left(\frac{\partial^2 V}{\partial Q_k \partial Q_l}\right)_0 Q_k Q_l + \cdots$$

some of the $\left(\frac{\partial V}{\partial Q_k}\right)_0$ may have non-zero values. Thus V does not have an extremum at the symmetric configuration and may be lowered by moving along the normal mode Q_k if the integral $\langle \Psi_\Gamma | Q_k | \Psi_\Gamma \rangle$ is non-zero. From group theory, this may occur when Q_k is contained in $[\Gamma^2]$, the symmetric direct product. (Similarly, a non-degenerate state, $\psi_{\Gamma'}$, may distort by interacting with a nearby state, $\psi_{\Gamma''}$, if the integral $\langle \Psi_{\Gamma'} | Q_k | \Psi_{\Gamma''} \rangle$ is non-zero. This process is known as the pseudo Jahn-Teller effect[2] and will not be the focus of this seminar.) For octahedral and tetrahedral molecules, an E state is split by an E mode and a T_1 or T_2 state by an E or a T_2 mode. The distortion will be largest if orbitals contributing to σ bonding are involved, i.e., e orbitals in octahedra and t_2 in tetrahedra.

Consider the simplest case--an E state (e.g., d^9 octahedral Cu(II)). Tetragonal distortions along the x, y, and z axes are equivalent and may be expressed as linear combinations of the two E normal modes. Thus, the potential energy surface in "E space" has three wells. If the vibronic wavefunction of the molecule is frozen in any one well, it exhibits a static Jahn-Teller distortion; however, if it surmounts the barrier between wells rapidly on the time scale of an experiment, it is dynamic.

Experimental verification of the static Jahn-Teller effect (SJT) may come from crystal structures, anisotropy in the ESR g and A tensors, electronic absorption spectra, and the Mössbauer quadrupolar splitting.[3,4,5,6] However, for the dynamic effect (DJT), most of this evidence will average to zero due to its very nature. The literature has many claims of DJT distortion based on scanty evidence.

There are several ways to detect DJT, however. First, one can try any of the above experiments at low temperature in an attempt to "freeze out" the distortion. It may at least be possible to see line broadening as the exchange slows. Second, the electronic absorption and photoelectron spectra will be altered because the distortion splits the degenerate state into several levels. Third is manifestations of the Ham effect, put forth in 1965 and described as follows.[7] The vibronic wave functions undergoing DJT must be quantized along the distortion axis. A perturbation which is not quantized along this axis (e.g., spin-orbit coupling or a trigonal distortion in a tetragonally distorted JT state) will be quenched. This can be seen by evaluating

off-diagonal elements of the perturbation Hamiltonian $\hat{H}_1$ in the JT distorted vibronic basis:

$$\langle \Psi_i | \hat{\mathcal{H}}_1 | \Psi_j \rangle = \langle \psi_i^{el} \phi_i^{vib} | \hat{\mathcal{H}}_1 | \psi_j^{el} \phi_j^{vib} \rangle = \langle \psi_i^{el} | \hat{\mathcal{H}}_1 | \psi_j^{el} \rangle \langle \phi_i^{vib} | \phi_j^{vib} \rangle = H_{ij}\, \gamma$$

The interaction H_{ij} expected in the absence of JT distortion is reduced by a factor, γ, the overlap of two equivalent non-orthogonal distortions. Thus, if one finds the magnitude of some perturbation, say spin-orbit coupling, much smaller than predicted for his spectrum, he has evidence for the DJT effect.

Most experimental claims for the JT effect are for octahedral Cu(II), where distortion is known to be large for many systems.[8,9] Joesten and coworkers[10,11] have studied the low-temperature ESR and room-temperature ESR and crystal structure of several tris-diphosphonate complexes of Cu(II). They postulate SJT-DJT to explain their results. While this is probably justified, they should have waited for the low-temperature crystal structure, which is forthcoming. They never mention the Ham effect due to the trigonal distortion of the octahedron by the bidentate ligand, and then criticize authors who postulate DJT in other non-octahedral systems. This appears somewhat inconsistent.

DJT has been used to successfully explain spectroscopic data on metals other than copper. Ham and Slack[12] employed it in an absorption-fluorescence study of tetrahedral Fe(II) doped into ZnS. Ammeter and Swalen[13] have explained the optical and ESR spectra of cobaltocene in terms of DJT and the Ham effect. A final example is the work of Gray and coworkers[14] on the absorption spectra of low-spin trigonal bipyramidal Ni(II), Pd(II), and Pt(II).

The dynamic Jahn-Teller effect has proven quite useful in interpreting spectral data. Unambiguous evidence for its existence is often lacking, but careful use of the techniques described here should lead to reliable conclusions.

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TRIMERIC TRANSITION METAL COMPLEXES WITH OXO AND NITRIDO BRIDGES

Rudolph Jungst May 15, 1973

Oxide and nitride are both strong donor ligands and form complexes of similar geometry in many cases. Polynuclear complexes with these bridging groups tend to be stable even in solution and often undergo chemical reaction without alteration of the "core" of the molecule. This makes possible the study of clusters of metal atoms under conditions of the same general geometry and often in various combinations of valence states. Particular attention in this seminar will be directed toward complexes with discrete trimeric units containing group VIII metals. Two geometries are found for this type of compound, a triangular structure with a single bridge atom and a linear arrangement with two bridging atoms.

One of the earliest examples of the triangular geometry was found in basic metal acetates, although at first these were formulated incorrectly as $[M_3(OAc)_6(OH)_2]^+$ species. From the properties of the chromium complex, Orgel suggested in 1960 that both the chromium and iron basic acetates had a planar arrangement of three metal atoms around an oxo bridge.[1] Interaction between metal centers could occur via the bridge, but the direct distance between the metals would be too long for a bond. This was subsequently borne out by the crystal structures.[2,3] Investigation of the magnetic properties of the iron and chromium compounds has shown the metal atoms to be antiferromagnetically coupled and determinations of the magnetic moments in solution indicate the trimeric unit is still present.[4] Duncan and coworkers concluded from further magnetic studies that the best fit to the observed susceptibilities was obtained by considering the exchange integral between two of the metal sites to be different from that to the third site.[5] Crystal structures, however, do not reveal any difference in the iron environments. The iron complex can also be prepared as a mixed valence compound formally containing two iron(III) and one iron(II).[6] Mossbauer spectra over a range of temperatures show the two different iron sites at 77° K., but at room temperature rapid electron transfer results in their being indistinguishable.[7] An interpretation of the magnetic properties of this complex has been proposed.[8]

Oxo and nitrido iridium sulfate complexes have also been studied extensively. In 1909, Delepine reported a green product isolated from the reaction of $(NH_4)_3IrCl_6$ with concentrated sulfuric acid.[9] This has been assigned the formula $K_4[Ir_3N(SO_4)_6(H_2O)_3]$ and the crystal structure of the ammonium salt shows it to have a nearly planar Ir_3N unit.[10] Oxo complexes result if no ammonium ions are present during preparation and these are assumed to have a similar structure. All combinations of valence states for iridium are known from three Ir(III) to three Ir(IV) for this complex.[11] The mixed valence compounds can be designated as class II systems using the classification scheme of Robin and Day.[12] Harrison and Logan have claimed preparation of an analogous iridium complex with nitrate.[13]

Other examples of triangular oxo bridged species have been found recently with the metals ruthenium and rhodium.[14,15] While evidence for the rhodium complex is rather scanty, the ruthenium trimer has been well characterized and undergoes two reversible one electron reductions to form products where the Ru_3O skeleton is still intact.

Ruthenium red is representative of the complexes with linear structures. It was studied in detail by Fletcher and coworkers who proposed the formulation $[(NH_3)_5Ru\text{-}O\text{-}Ru(NH_3)_4\text{-}O\text{-}Ru(NH_3)_5]Cl_6\cdot 4H_2O$ on the basis of conductivity and spectral properties.[16] A crystallographic examination of the analog with two ethylenediamines on the central ruthenium has shown the Ru-O-Ru angle to be 177°.[17] Ruthenium red is readily oxidized in a one electron step to ruthenium brown in which the basic structure appears to be unchanged. Ruthenium Mössbauer studies support the present formulation of the complexes.[18] The kinetics of the oxidation of hydroxide by ruthenium brown indicates the rate determining step may be attack of hydroxide at the central metal atom in the chain.[19] This reaction has been shown to follow the same rate law for both ruthenium brown and its ethylenediamine analog. A compound which has been proposed to have a structure related to that of ruthenium red is the product of the reaction of osmium tetroxide with liquid ammonia. Cleare and Griffith have interpreted infrared spectra and chemical properties to imply a linear arrangement of three osmiums with two nitrido bridges.[20]

In conclusion, it should be noted that the triangular complexes in particular are a rather general type of compound, being found also for the metals vanadium, manganese, and aluminum as well as those already mentioned. They thus form a useful series for the investigation of metal interactions in clusters.

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